JOURNAL OF APPLIED ELECTROCHEMISTRY **26** (1996) 1117–1123

Preparation and evaluation of electrocatalytic oxide coatings on conductive carbon–polymer composite substrates for use as dimensionally stable anodes

A. BRUNGS, V. HADDADI-ASL, M. SKYLLAS-KAZACOS

School of Chemical Engineering and Industrial Chemistry, University of New South Wales, Sydney, NSW 2052, Australia

Received 23 August 1995; revised 21 March 1996

This work investigates the feasibility of developing a lower cost dimensionally stable anode based on a polymer substrate by examining possible methods of applying coatings, such as MnO_2, to catalyse the oxygen evolution reaction. The conductive polymer is based on a blend of polypropylene and a rubber, to provide the mechanical strength and acid resistance of the electrode, with graphite fibre and carbon black dispersed through the composite to ensure a reasonable conductivity. Of the different compositions analysed, the best incorporated Degussa XE-2 carbon black. This material not only displays an overpotential at its bare surface which was comparable to the lead electrode, but also it provides excellent contact with the catalyst coatings. Two methods of applying a catalytic coating, thermal decomposition and pressed oxide coating, are evaluated. Coatings prepared by thermal decomposition displays an overpotential greater than the standard lead electrode, although the poor performance of the catalysts is found to be due to poor contact with the conductive sites of the substrate and to incomplete thermal decomposition of the metal chlorides to the oxide. The pressed oxide coating method is the technique developed during this work to take advantage of the properties of the polymer composites. Polymer substrates are heated until soft and the MnO_2 catalyst (in its active form) is pushed into the surface. Electrodes coated in this manner with MnO_2 all display excellent overpotentials which, on average, are 0.2 V less than the lead electrodes. Extension of this technique to the coating of polymeric substrates with other catalytic oxides shows great potential.

1. Introduction

In industrial electrolytic processes such as zinc electrowinning, a considerable amount of energy is expended in overcoming the high overpotential of the oxygen evolution reaction at the anode. Due to the commercial significance of this problem, much research has been conducted into reducing this overpotential. Most systems currently proposed utilize a dimensionally stable anode (DSA$^{®}$) based on a titanium substrate coated with a material which is catalytic towards oxygen evolution.

The most common valve metal base used for DSAs is titanium. Such electrodes, however, exhibit very poor performance when used as oxygen evolving anodes [1]. Studies have been conducted to ascertain the most efficient base material. However, these studies have almost exclusively concentrated on valve metals, such as titanium, tantalum, zirconium, niobium, hafnium and tungsten [1–3]. These materials develop a very corrosion resistant non electrically conductive oxide or barrier layer. They are thus able to retain their dimensional integrity during service. However, these layers, being non-conductive, prevent the material's use as an anode. An electrochemically active and conductive metal oxide is thus used to coat the electrode surface. The resulting anode should be both electrolytically active and stable.

Comninellis and Vercesi [1] conducted a detailed investigation of various (Ti, Zr, Ta, Nb) valve metal bases. The results showed that tantalum best meets the prerequisites for a stable conducting base while zirconium fared extremely poorly. Tantalum, however, is extremely expensive and thus, on a cost/performance basis, titanium represents the best overall alternative. Very little work has been carried out on other types of electrode substrates such as conductive polymers composites, even though these materials are being successfully employed in a number of applications such as batteries [4, 5].

1.1. *Conductive oxide coatings*

The most important aspect of a DSA is the electrocatalytic coating used on the surface. This coating not only enables electrical charge transfer between the base metal and the electrode/electrolyte interface, but it must also catalyse the desired reaction. The major problem with most electrocatalysts, however, is that they have limited stability and consequently degrade fairly rapidly in the working solution. To increase the stability of these catalyst, non-conductive

0021-891X

or semiconducting stabilizing oxides, such as TiO_2, SnO_2, TaO_2, ZrO_2 etc. are added.

It is very important to note that the mechanism of oxygen evolution is independent of the presence of a stabilizing oxide in the coating. Although the exchange current density and the electrocatalytic activity of the electrode decrease as the concentration of stabilizing oxide grows, the basic mechanism, shown by the Tafel plot, remains constant. This confirms that the stabilizing oxide plays no role in the oxygen evolution and serves only to increase the stability of the coating [1].

1.2. *Oxide coatings of conductive polymer composite for acidic environments*

Conductive polymer composites composed of graphite fibre, carbon black and polyolefin, are already widely used in the development of new battery systems but to date, have not been considered as electrode substrates for other industrial electrochemical applications. Graphite–polyethylene (PE) composite electrodes have already been very successfully used in the vanadium redox cell [5, 6] and energy efficiencies of up to 90% have been achieved in 1 kW prototype vanadium batteries employing conducting polymer composite electrodes [7]. Similar materials have also been developed for the Zn/Br_2 battery [8].

To function adequately as a base for a dimensionally stable anode the polymer composites must possess the following important characteristics: good stability under oxygen evolution conditions, maintenance of dimensional integrity, stability in acidic electrolytes, good conductivity, low cost, mechanical integrity, and allow good electrical contact with electrocatalytic coating.

Zhong and co-workers [5] analysed various compositions of low density PE, carbon black and graphite fibre. They concluded that conducting plastic materials with resistivity as low as 0.13 Ω cm could be fabricated, and that these materials showed considerable stability in acidic solutions during voltametric cycling. Various compositions were analysed and the combination of graphite fibre, graphite powder and carbon black was tested for resistivity.

The most conductive composite was composed of low density PE 50%, graphite fibre 25% and carbon black 25% with a resistivity of 0.13 Ω cm. However, the presence of high levels of graphite fibre in these composites caused problems with sheet extrusion such as high levels of abrasion of the die. Further work led to promising results with blends of polypropylene, ethylene–propylene rubber, carbon black and graphite fibre [9]. Such composites could thus be made electrochemically active by application of an electrocatalyst metal oxide layer.

The purpose of this work is to investigate the feasibility of employing a conductive polymer as a substrate for dimensionally stable anodes, and to examine possible methods of applying oxide coating to catalyse the oxygen evolution reaction.

2. Experimental details

2.1. *Materials and procedures*

2.1.1. Materials. The following materials were used in the preparation of the composites:

Polymers: polypropylene (Propathene LZM60CR, ICI Co., Australia), ethylene–propylene rubber (EPR) (Vistalon 404, Exxon Co., Australia), butyl rubber (Exxon Chemicals, Australia) and isobutylene-co-high density polyethylene (BMX-42 Vistaflex Esso Chemicals Australia).

Carbon black: Vulcan XC72 (Cabot Corp., USA) and Printex XE-2 (Degussa Co., USA).

Graphite fibre: Kureha C-203s (3 mm, Kureha Co. Ltd., Japan).

Metal mesh: 100 mesh (150 μm) brass mesh (Swiss Screen Pty, Ltd., Australia).

Metal oxides, salts and chemicals: MnO_2, SnO_2, H_2IrCl_6, $MnSO_4$, $TaCl_5$, dry ethanol (99.7%) and isopropanol (Aldrich Chemicals, Australia).

Release oil: 20 release coating (Dow Corning Australia Pty, Ltd., Australia).

2.1.2. Preparation procedure. Although both polyethylene (PE) and polypropylene (PP) can be used for composite preparation the present work deals only with PP based materials. The polypropylene was pre-mixed in a 'Haake 600' internal mixer with the elastomer for 5 min followed by 10 min mixing with conductive carbon black. Graphite fibre, if required, was then added slowly for 20 min. The mixture was pressure-moulded by a 'Stacy' hydraulic 40 tonne press with 250 kg cm^2 pressure at 200 °C for at least 30 min. A metal mesh sheet (as a current collector) was placed below the composite sheet inside the mould and the mould was heated up to 200 °C for 20 min. The mould was then cooled down under pressure. The sheets were removed from the mould and the back sanded with P80 and P1200 grit sandpaper to ensure complete exposure of the copper. The individual electrodes were manufactured in the following manner:

(i) Discs 1.2 cm in diameter were cut from the circular copper mesh/composite sheets using a hole punch.

(ii) Insulated copper wire was soldered to the copper mesh current collector at the back of the discs.

(iii) The electrode was enclosed in epoxy leaving the face of the disc free. Several coats of epoxy resin were applied to ensure that no flaws due to air bubbles would allow electrolyte to contact the copper mesh on the back of the electrode.

(iv) The resistance of each electrode was determined. Only electrodes with resistance less than 2–4 Ω were employed in the polarization studies.

2.2. *Resistivity measurement of composite sheets*

The resistivity of the composite sheets with the copper backing, was measured by placing them between two 10 cm × 10 cm copper plates. The current between the

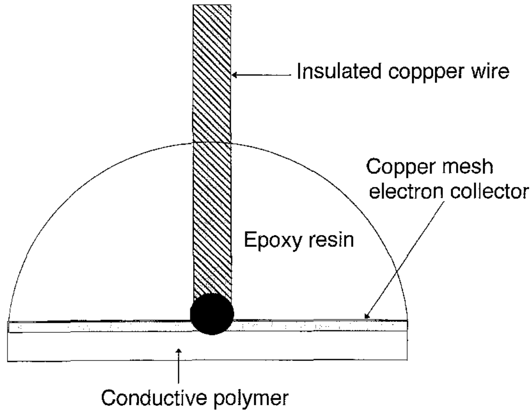

Fig. 1. Electrode design.

copper plates was varied and the voltage drop measured over a wide range of values enabling the area resistivity to be calculated from:

$$R = A\frac{V}{I}$$

where R is the area resistivity ($\Omega\,\mathrm{cm}^2$), V is the potential difference (V), I is the current (A) and A the geometric area of specimens (cm^2).

2.3. *Three-electrode cell*

A three-electrode cell (Fig. 2) was used for analysing the electrochemical properties of the coated and uncoated plastic composite electrodes. The solution used was 1.5 M H_2SO_4 and a graphite rod and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The conducting polymer working electrode fabricating is illustrated in Fig. 1.

2.4. *Voltammetry*

A RDE3 Pine potentiostat/galvanostat was used for linear sweep voltammetry. The potential was varied at a rate of $0.3\,\mathrm{V\,min^{-1}}$ from 1 V to 3 V vs SCE and the current/voltage responses were recorded using a Riken Denshi X–Y recorder. Great care was taken in selecting the scan rate. If the scan rate was too slow, the electrode surface became blocked by the evolved oxygen bubbles, while too fast a scan rate gave the electrode insufficient time to reach equilibrium. A rate of $0.3\,\mathrm{V\,min^{-1}}$ appeared to be the best compromise. The voltammetric response of each electrode was recorded in duplicate to ensure good reproducibility of results. To minimize the interfering effects of the evolved oxygen bubbles on the horizontal electrodes, the solution near the electrode was agitated by a stream of oxygen gas.

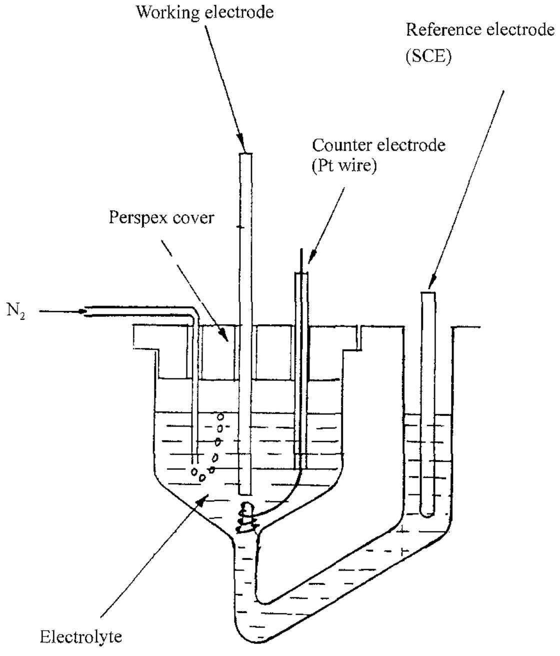

Fig. 2. Three-electrode cell.

2.5. *Coating method*

2.5.1. Pressed oxide coating. MnO_2 and SnO_2 were used to fabricate the pressed electrodes. A wide variety of techniques for applying the pressed oxide coatings were evaluated before a suitable method was found. The following outlines the final procedure.

(a) To produce ‘penetrated’ oxide crystal coatings:
(i) From the square composite sheets, 1.5 mm thick, a 7.9 cm diameter circular disc was cut.
(ii) A light release agent oil was applied to the surface, to enable the oxide to adhere to the disc during handling before heating.
(iii) A known weight ($1.5\,\mathrm{mg\,cm^{-2}}$) of catalyst was spread evenly over the surface of the disc.
(iv) The disc was placed, along with its corresponding piece of copper mesh into the circular mould (depth, 1 mm).
(v) The mould was heated for 40 min at 200 °C.
(vi) A pressure of $250\,\mathrm{kg\,cm^{-2}}$ was applied to the mould for 30 min while maintaining the temperature at 200 °C. Since the sheet thickness was greater than the mould depth, the catalyst particles were pushed into the plastic.
(vii) The pressure was released, and the plastic was allowed to cool down to ambient conditions over a 2–3 h period. The mould was then opened and the catalyst coated discs were removed. In the process the thicker plastic sheet is pressed to a smaller thickness and larger diameter disc. As a result, the oxide crystals penetrate the composite surface to 2/3–3/4 of their length.

(b) To produce ‘surface’ oxide crystal coatings the same method was used as in (a), except that 1 mm thick composite discs were employed. The oxide coated disc was placed into the circular mould and heating to 180 °C with a pressure of $250\,\mathrm{kg\,cm^{-2}}$. Since the sheet were the same thickness as the mould, the catalyst particles were not pushed too deeply into the composite surface.

The oxide powder coatings were either MnO_2 or a MnO_2/SnO_2 mix. The discs were then used to fabricate electrodes as previously described.

3. Results and discussion

3.1. *Plastic composite evaluation*

Composites of various compositions were initially prepared and if the mechanical and electrical properties were acceptable, the electrochemical properties were then assessed by linear sweep voltammetry, followed by stability tests of the most promising coatings. Linear sweep voltammetry was used to first determine the overpotential of the oxygen evolution reaction (OER) on the bare composite surface. This provided a datum point against which the coated electrodes could be compared. In the present study the OER was studied in sulfuric acid solutions. Further evaluation in basic media is being undertaken as a separate study.

3.1.1. Composite sheet fabrication. During the initial stages of this work, a large number of plastic composites was investigated. As mentioned earlier, conducting plastic composites possessing the desired properties for electrode preparation, can be successfully prepared using either PP or PE. In the present work, however, only electrodes based on PP will be described. Of the PP-based formulations trialed, only six had adequate mechanical (i.e., not brittle) and stability properties as well as sufficient conductivity to warrant further investigation. These six composites, details of which are given in Table 1, were subjected to linear sweep voltammetry to evaluate their electrochemical properties.

A constant loading of 40% polypropylene (PP) was added to all the composites. This level was based on previous research [9], and was sufficient to give the composite excellent stability in the acidic environment. Rubber, such as ethylene–propylene rubber (EPR), butyl rubber (BR) and isobutylene-co-HDPE (BMX-42), was used to increase the impact strength and flexibility of the composite. Without a sufficient loading of rubber, the plastic composite was brittle and broke easily upon handling. Carbon black (CB), and graphite fibre (GF) provided the conducting base for the composite. However, as the rubber loading was increased the conductivity decreased. This has been attributed to the lowered crystallinity of the composite which leads to a lowering of the orientation of the conductive fillers [4]. Thus a trade-off between properties was required. The graphite fibre content was perhaps one of the most crucial ingredients. At a minimum loading of 20% an electrical network of graphite fibre is allegedly created [5], greatly increasing the conductivity. High graphite fibre loadings are however, detrimental to the processing of the material and should thus be kept to a minimum. The carbon black loading was varied between 20–40%. In one composite a special grade of highly conductive Printex XE-2 carbon black was added to see if there was any effect on the oxygen overpotential. However, although the increased content of this type of carbon black resulted in higher conductivity, its processing became very difficult.

3.1.2. Linear sweep voltammetry at bare composite substrates. Linear sweep voltammograms were obtained for each of the six composites plus a lead dioxide electrode. To minimize interferences caused by the evolution of bubbles on the electrode surface, oxygen was sparged over the surface to assist in their removal. From the voltametric scans presented in Fig. 3, it can be seen that the oxygen overvoltage values at a current density of 15 mA cm^{-2} on the different composites are distributed over a range of about 0.4 V. The lowest oxygen overvoltage was obtained with the composite containing Printex XE-2 carbon black (sample 2).

There are two effects which would alter the nominal overpotential of an electrode measured by linear sweep voltammogram. The first is actual catalytic activity. The second is surface area and morphology. It has been suggested [10] that while neither graphite fibre nor carbon black is particularly catalytic towards the OER, each type of carbon possesses differing types and amounts of active sites. Differences in apparent oxygen overpotential are therefore attributed to variations in surface activity and overall active surface area. The number of active sites will be different for different types of carbon.

3.1.3. Effect of graphite fibre content. The graphite fibre loading of the composite was varied to determine its effect on the overpotential. From Fig. 4, it is apparent that the higher the loading of graphite fibre for a constant total carbon content,

Table 1. Polymer compositions (with 40% polypropylene)

Sample	*Composite*/wt%						*Volume resistivity* /Ω cm
	Rubber content			*Conductive filler content*			
	EPR	*BMX-42*	*BR*	*Vulcan XC72*	*Graphite fibre*	*Printex XE-2*	
1	20	–	–	20	20	–	0.29
2	20	–	–	20	10	10	0.13
3	20	–	–	40	–	–	0.54
4	20	–	–	35	5	–	0.36
5	–	20	–	20	20	–	0.12
6	–	–	20	35	5	–	0.34

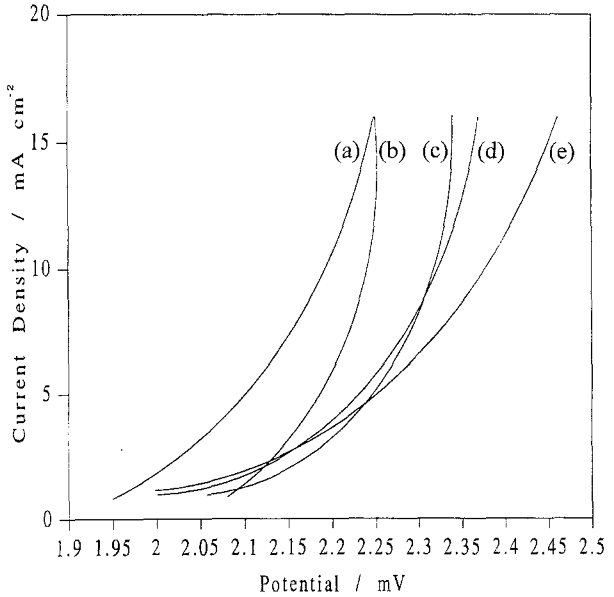

Fig. 3. Linear sweep voltammograms of polymer composites in 1.5 M H_2SO_4 electrolyte (composition as described in Table 1). Key: (a) XE, (b) CB-40%, (c) BMX, (d) GF-5% and (e) BR.

the lower the oxygen overpotential obtained. This shows a difference between carbon black and graphite fibre with respect to the oxygen evolution reaction. The lower overvoltage observed on the high graphite fibre material may be associated with two possible effects. First, the graphite fibre is more exposed on the surface with higher overall surface area for oxygen bubbles to be formed and released at these sites. Second, graphite fibre may be more electroactive than carbon black for the oxygen evolution reaction. However, as the graphite fibre content is increased the processing properties of the electrode are reduced. Thus, an optimum level which maximizes both electrochemical activity and processing property must be determined.

3.1.4. Plastic etching. From the previous sections it would appear that a major factor in the OER on uncoated polymer composites is in fact the surface area of the exposed graphite fibre. All the polymer composites were thus etched for varying periods in a chromic acid solution to remove the polymer surface layer and increase the exposure of the graphite fibres, increasing their effective surface area. This was done for two reasons, to confirm the dependence of nominal overpotential on surface area and to produce electrodes with lower overpotentials. Figure 5 depicts composite 1 and the typical trend of results for all the composites. Composite 1 was etched in chromic acid for 20 min and 50 min periods.

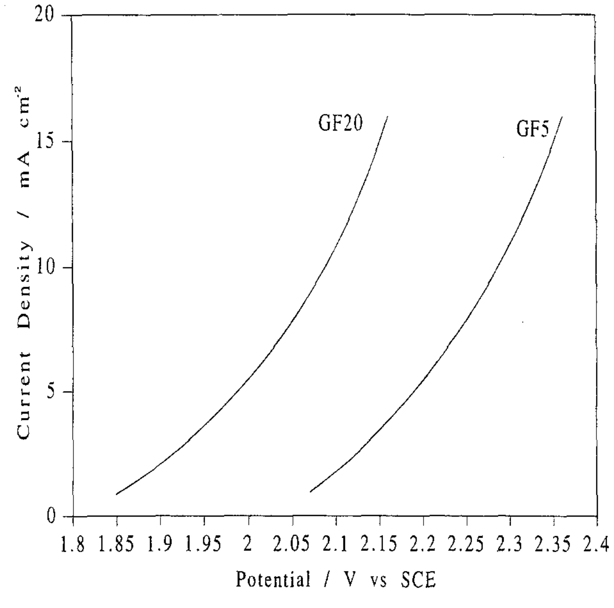

Fig. 4. Effect of graphite fibre loading on the electrochemical properties of electrodes in 1.5 M H_2SO_4 solution.

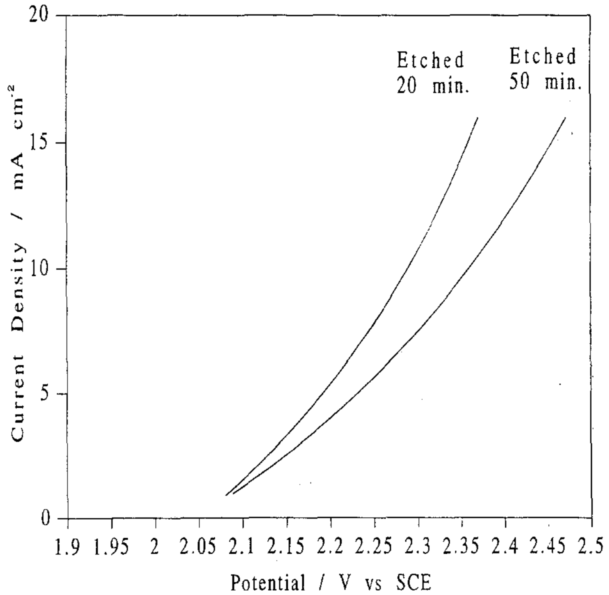

Fig. 5. Effect of etching upon overpotential behaviour of polymer composite in 1.5 M H_2SO_4 solution.

The nominal overpotential actually increases with the degree of etching. While this was an unexpected result, careful observation of the electrode during electrolysis revealed that the increase in surface area brought about a corresponding increase in the overall 'roughness' of the electrode as well as exposing a greater amount of the graphite fibres all closely interwoven with each other. During electrolysis the oxygen bubbles evolved tended to adhere more firmly to the rough horizontal electrode surface and were very difficult to dislodge even with oxygen sparging. The increase in overpotential is thus primarily due to an increase in bubble polarization as the presence of oxygen bubbles reduces the contact area between the solution and the electrode surface.

It can thus be concluded that etching to expose graphite fibres to increase the composite active surface area is unsuitable for these horizontal oxygen evolving electrodes, although the results would be different for vertical electrodes.

3.2. *Electrocatalytic coatings*

Due to its stability and excellent mechanical properties (i.e., flexibility) coupled with a very low electrical resistivity, composite 2 was chosen as the primary substrate for further analysis as an oxide coated DSA. The catalyst selected for evaluation in this work, was MnO_2. Although MnO_2 would be expected to be unsuitable for oxygen evolution in an acidic electrolyte, because of its low cost compared with more suitable catalysts such as IrO_2 and RuO_2, it was selected for these preliminary studies aimed at developing appropriate coating techniques for the polymer composite substrates.

MnO_2 of approximately 200 μm particle size was thus evaluated as a catalyst using the pressed oxide coating technique. The catalyst was spread onto the surface of the composite at a loading of 1.5 mg cm^{-2}. This level was consistent with loadings reported by Comninellis and Vercesi [1]. To enable the catalyst to adhere to the substrate before heating, a light release oil (Dow Corning 20 release oil) was used to coat the composite. The volatility of the oil was such that during the heating phase it should have completely vaporized off the electrode. The application technique was varied such that two types of coating were obtained. In the first approach, subsequently referred to as type 1 or 'penetrated MnO_2', the MnO_2 was pushed 1/2–3/4 of its particle length into the composite surface. The second type of coating referred to as type 2 or 'surface MnO_2', had the MnO_2 catalysts only superficially embedded in the composite. This was sufficient to provide good electrical contact, but left the bulk of the MnO_2 crystals free of the plastic.

The type 1 electrode, where MnO_2 was deeply embedded into the XE composite, displayed an oxygen overpotential of approximately 0.2 V less than that of the lead oxide electrode within the current density range 0–16 mA cm^{-2}. As seen in Figs 6 and 7, not only was there a change in the absolute value of the overpotential, but the Tafel slopes of two electrodes were slightly different. This can be attributed to either a change in the mechanism for oxygen evolution for each electrode, or to the fact that the different surface morphologies might have varying degrees of entrapped oxygen resulting in different levels of bubbles resistance during the polarization measurements.

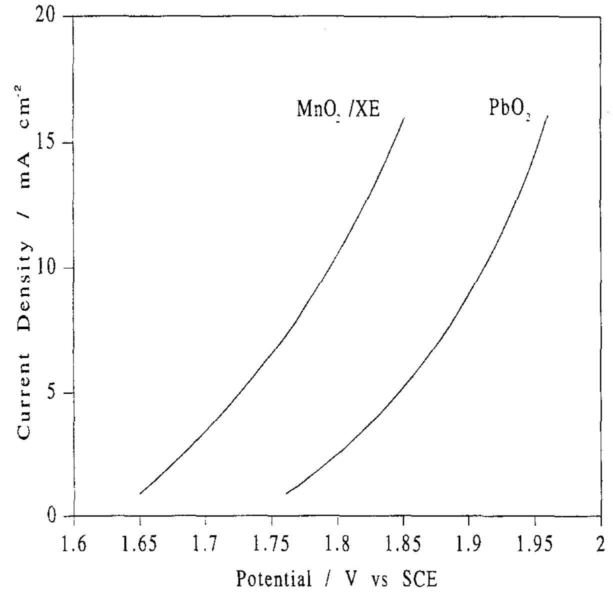

Fig. 6. The overpotential behaviour of PbO_2 and type 1 MnO_2 electrodes in 1.5 M H_2SO_4 solution.

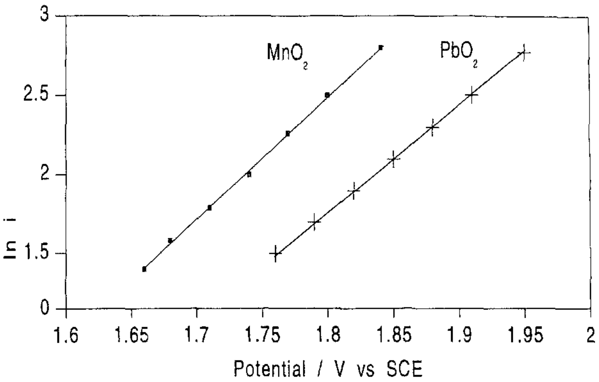

Fig. 7. Tafel plot of the PbO_2 and type 1 MnO_2 electrodes using I/V data from Fig. 6.

The current–voltage behaviour of the electrodes composed of MnO_2 crystals superficially embedded in the XE composite (i.e., type 2) is given in Fig. 8. Although the initial scan obtained with this electrode showed a slightly lower overvoltage than for the type 1 MnO_2 coating, after being subjected to extended oxygen evolution for 1 h, the perforation deteriorated considerably as shown in Fig. 8. In fact, after another 2 h of oxygen evolution, the measured overpotential was not significantly different from that of the base composite. In contrast, the type 1 MnO_2 electrode, when subjected to similar periods of oxygen evolution, showed no change in overpotential (see Fig. 8).

It would appear that the mechanical action of the oxygen bubbles on the type 2 MnO_2 coating was sufficient to knock the partially embedded crystals from the composite. This was confirmed by optical microscopy which showed the surface of XE composite

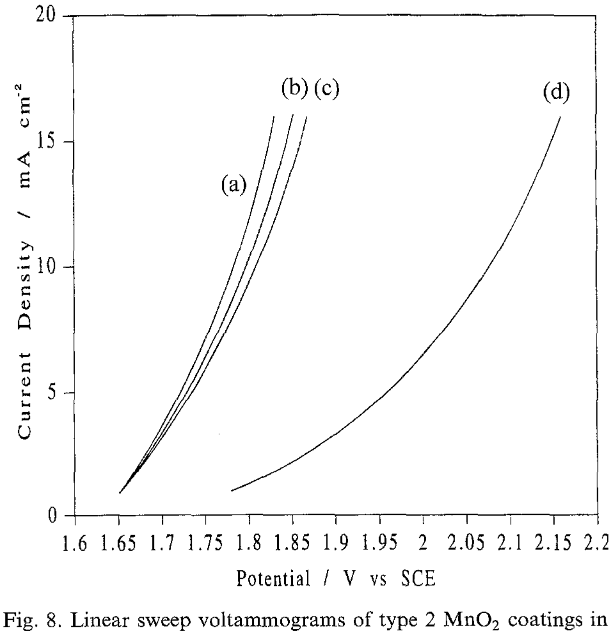

Fig. 8. Linear sweep voltammograms of type 2 MnO_2 coatings in 1.5 M H_2SO_4 solution before and after extended cycling. Key: (a) type 2 surface MnO_2, (b) type 1 MnO_2, (c) cycled type 1 MnO_2 and (d) type 2 surface cycled MnO_2.

covered with holes where MnO_2 crystals had been dislodged. The earlier analysis of results for the composite electrodes studied showed that amongst the bare composite substrates, XE composite (composite 2) gave the best performance as an oxygen evolution electrode. The substrate for a DSA does not itself have to possess a low overpotential however, in fact, in this case, it would appear that this could be detrimental to the stability of the coated electrode. If the substrate has a similar overvoltage for oxygen evolution as the coating, the presence of pin holes in the coating could lead to oxygen evolution at the substrate surface. The evolution of oxygen bubbles thus formed would cause mechanical wear on the oxide coatings. Thus the stability of the entire electrode would be reduced. The Tafel slope of both the electrodes with type 1 MnO_2 and the initial results for the type 2 surface MnO_2 electrodes, however, were similar, indicating that, as expected, the mechanism of oxygen evolution is similar at the two electrodes. The type 2 surface MnO_2 initially displayed marginally lower oxygen overpotentials due to the increased surface area presented by the highly exposed MnO_2 crystals.

4. Conclusions

The present study evaluated the feasibility of the pressed oxide technique for preparing electrocatalytically active coatings on conducting polymer composite substrates for the fabrication of DSAs for the oxygen evolution reaction. Promising results were obtained with MnO_2 coatings hot pressed into a carbon–polypropylene composite substrate. The overpotential of these electrodes was 0.2 V lower at $16\,mA\,cm^{-2}$ than that of the lead anode system which is currently used in several industrial electrolysis processes such as zinc electrowinning.

Although MnO_2 is not the ideal anode coating material for acidic electrolytes, the use of the conducting polymer substrate and the technique of pressed oxide coating appear to be extremely useful and worthy of further investigation. Other oxides such as IrO_2, RuO_2, TiO_2, SiO_2 and mixtures of these require investigation as potential stable catalytic coatings for the conductive polymer composite substrates.

References

[1] C. H. Comninellis and G. P. Vercesi, *J. Appl. Electrochem.* **21** (1991) 335–45.

[2] V. DeNora, *US Patent 4 302 321* (1981).

[3] H. B. Beer, *US Patent 3 632 498* (1972).

[4] V. Haddadi-Asl, M. Kazacos and M. Skyllas-Kazacos, *J. Appl. Polymer Sci.* **57** (1995) 1455.

[5] S. Zhong, M. Kazacos, M. Skyllas-Kazacos and V. Haddadi-Asl, *International Patent WO 94/06164* (1994).

[6] V. Haddadi-Asl, M. Kazacos and M. Skyllas-Kazacos, Proceedings of the 9th Australian Electrochem. Conference, Wollongong, NSW, Australia (1995) p. 64.

[7] M. Skyllas-Kazacos, D. Kasherman, D. R. Hong and M. Kazacos, Proceedings of the Solar '89 Conference Australian and New Zealand Solar Energy Society, Brisbane, Australia, **2** (1989).

[8] Gould Inc., 'Development of Zinc Bromine Batteries for Stationary Energy Storage', EPRI EM-2497, July (1982).

[9] V. Haddadi-Asl, M. Kazacos and M. Skyllas-Kazacos, *J. Appl. Electrochem.* **25** (1995) 29–33.

[10] G. L. Cahen, *J. Electrochem. Soc.* **135** (1988) 368–72.